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Metallation reactions of diphosphiranes: new access to σ- and π-diphosphaallyl complexes

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Abstract

The metallation reactions of the functionalized diphosphiranes **1a,b** with the anionic metal transition complexes $Na[(Cp)_nM(CO)_m]$ (M = Mo, W, or Co) afford σ- or π-diphosphaallyl complexes depending on the substituents of the intracyclic carbon atom. The same complexes are also obtained from their photochemical isomers, the 1,3-diphosphapropenes **2a,b**. The complexes are thermally labile as shown by variable-temperature NMR spectroscopy. Upon heating, the σ-diphosphaallyl cobalt complex **3aC** is irreversibly transformed into the π-complex **4aC**. In contrast, with M = Fe and in toluene solution at reflux, reduced 1,3-diphosphapropenes **5a,b** are obtained. Further, the *gem*-dihalogenated diphosphiranes **1c,d** and their isomers **2c,d** lead quantitatively to 1,3-diphosphaallene **6** under the same metallation conditions. The mechanism of the coordination reactions is discussed.

1. Introduction

The availability of allylic complexes of transition metals from cyclopropanes has allowed great exploitation of these systems in synthetic and catalytic reactions [1]. The substitution of carbon for phosphorus atom(s) in the 3-membered rings allows η^1- and η^3-coordination without bond breaking, as well as formation of phosphaallyl complexes [2]. In the diphosphirane series, cyclic complexes were first prepared by Huttner [3] *via* the condensation of diphosphene complex with carbenoids. Related chemistry was reported by Weber [4] for the synthesis of transition-metal substituted diphosphaspiropentanes. More recent work of Stelzer [5] describes the reaction of methylene bis(dichlorophosphines) with $[Fe_2(CO)_9]$. All routes to η^1 cyclic complexes concern metallated starting materials and do not involve direct metallation of diphosphirane derivatives. The sole attempt to complex diphosphiranes is due to Seyferth [6] who obtained bridged iron complex in 10% yield. In 1990, we reported the first example of complex formation of functionalized diphosphiranes with transition metal complexes [7]. More recently, Jutzi allowed a ring diphosphirane to react with $[Cr(CO)_5THF]$ and obtained an η^1-diphosphirane pentacarbonyl chromium complex [8].

Starting from the previously described monohalogenated diphosphiranes **1a,b** [9] we report complexation reactions with anionic transition metal complexes, which constitute a new route to 1,3-diphosphaallyl complexes. The reactivity of the 1,3-diphosphapropenes, **2a,b**, obtained by photochemical ring-opening of the corresponding diphosphiranes [10] towards the same complexes is compared to that of the parent precursors.

2. Results

The reaction of the monohalogenodiphosphiranes **1a,b** with an excess (10 molar eq) of $Na[CpM(CO)_3]$ (**A**: M = Mo, **B**: M = W) in refluxing toluene for 18 h, afforded both η^1- and η^3-allylic complexes (30–40% yield) depending on substituents in the cycle (Scheme 1). For R = Me, **1a**, the reaction leads to the η^1-diphosphaallyl molybdenum or tungsten complexes, **3aA** and **3aB**, respectively. For R = Ph, **1b**, the η^3-diphosphaallyl complexes **4bA** and **4bB** are obtained.

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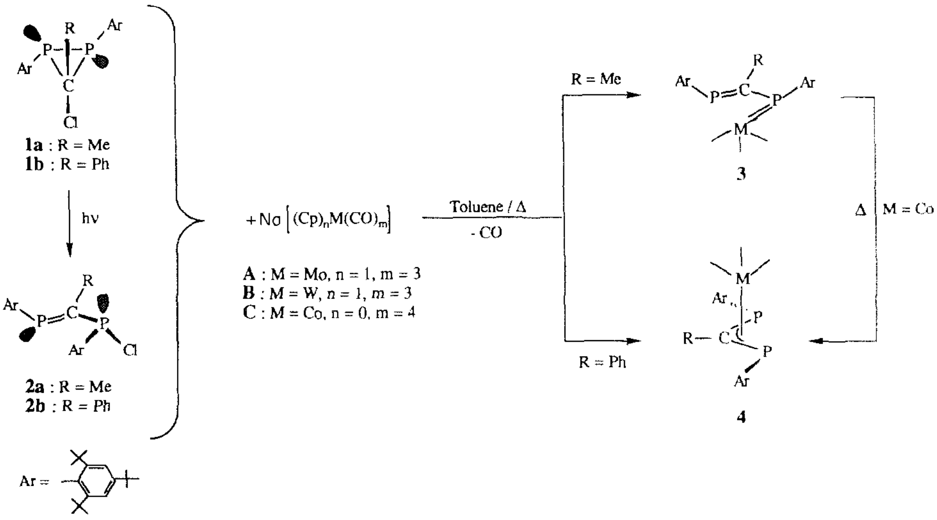
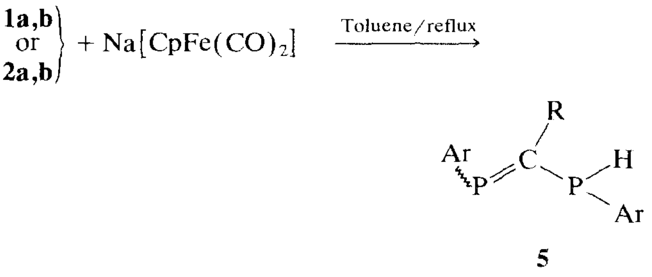


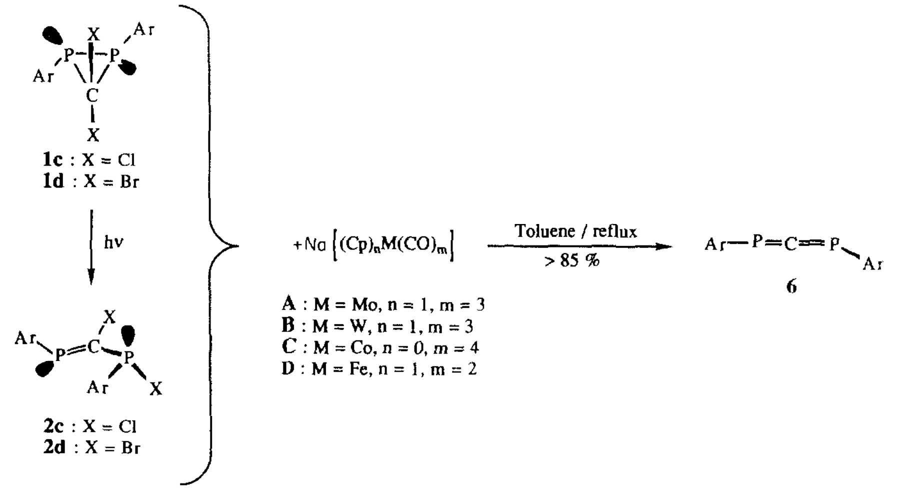
Scheme 1. Reactions of the functionalized diphosphiranes **1a,b** and 1,3-diphosphapropenes **2a,b** with the anionic metal transition complexes.



Scheme 2. Reactions of the functionalized diphosphiranes **1a,b** and their photochemical isomers **2a,b** with the dicarbonylcyclopentadienylferrate.

With the corresponding *P*-chlorodiphosphapropenes **2a,b**, complexation occurs more readily. The reaction with 4 h of warming does not require more than four equivalents of the anionic complexes. The same diphosphaallyl complexes **3** and **4** were obtained in 70–90% yield with the same selectivity as their parent diphosphiranes (Scheme 1).

With sodium tetracarbonylcobalt (4 molar eq) in toluene at reflux for 3 h, as with molybdenum and tungsten complexes, the η^3-diphosphaallyl complex **4bC** is obtained from **2b**. Treatment of **2a** with an excess of Na[Co(CO)$_4$], **C**, (4 molar eq) in THF at 45°C for 3 h



Scheme 3. Reactions of the *gem*-dihalogenated diphosphiranes **1c,d** and their photochemical isomers **2c,d** with the anionic metal transition complexes.

TABLE 1. ^{31}P NMR parameters of the η^1- and η^3-complexes **3** and **4** in C_7D_8 at 30°C

Complex	M	$\delta\ ^{31}P$	$^2J(PP)$	$^1J(PW)$
3aA	Mo	331 (P_A); 327 (P_B)	110 Hz	–
3aB	W	328 (P_A); 274 (P_B)	112 Hz	700 Hz
3aC	Co	350 (broad)	–	–
4bA	Mo	65	–	–
4bB	W	5.1	–	137 Hz
4bC	Co	64	–	–
4aC	Co	61	–	–

or in toluene at 50°C for 1 h affords the (η^1-diphosphaallyl) cobalt complex **3aC** in 30% yield (Scheme 1). However, upon heating in refluxing toluene for 3 h, the phosphidocobalt complex **3aC** is irreversibly transformed into the π-allylic complex **4aC**.

The 1,3-diphosphaallyl complexes are purified by filtration of the reaction mixture, evaporation of the solvent, and recrystallization of the residue from pentane. The (η^1-diphosphaallyl) complexes **3**, obtained as yellow oils, are unstable in solution upon standing and slowly undergo decomposition. Unlike **3**, the (η^3-diphosphaallyl) complexes **4** are stable and were purified as red powders. All compounds were characterized spectroscopically.

The complexation reactions do not take place with all the anionic transition metal complexes. Treatment of diphosphiranes **1a,b** with $Na[CpFe(CO)_2]$ in refluxing toluene solution yields the reduced 1,3-diphosphapropenes **5a,b** (Scheme 2). This suggests that under the reaction conditions, the dicarbonylcyclopentadienyl iron anion decomposes to reducing agent $[CpFe(CO)_2H]$ by H-abstraction from the solvent. Similar results were observed with the 1,3-diphosphapropenes.

On the other hand, the *gem*-dihalogenodiphosphiranes **1c,d** and their photochemical isomers **2c,d** react with all the anionic complexes mentioned above and give quantitatively 1,3-diphosphaallene **6**, whatever the nature of metal (M = Fe, Mo, W, or Co) (Scheme 3). No diphosphaallyl or cyclic complex intermediates could be detected.

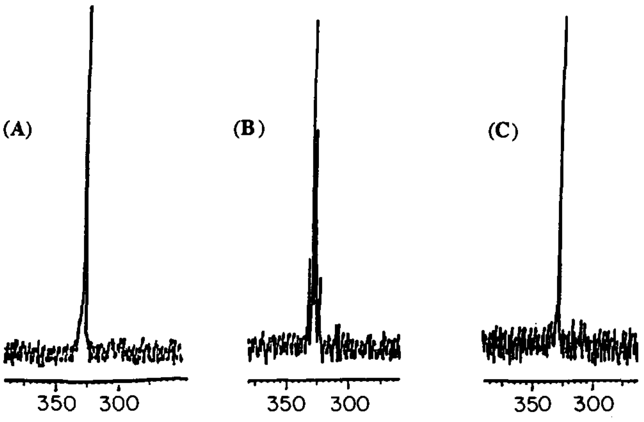
3. Discussion

We have previously reported the reactivity of diphosphiranes towards organolithium reagents [11], Grignard reagents [12], Lewis acids [13], oxidizing reagents [14], photochemical irradiation [10], and upon heating [14–16]. All these reactions involve the cleavage of the P–P bond, which is obviously the weakest bond in the three-membered ring. The diphosphaallyl cations generated by the reaction of Lewis acids with the diphosphiranes are unstable and lead instantaneously to cyclic phosphonium species [13]. The results reported here for the complexation reactions of functionalized diphosphiranes show that their behaviour towards the anionic transition metal complexes is also related to the ring-opening reactions, affording η^1- or η^3-diphosphaallyl complexes.

Karsch *et al.* [17] using another approach, reported the synthesis of analogous η^1-complexes **3** from the unsubstituted 1,3-diphosphapropenes. However, η^3-complexes **4** (Mo or W) were not formed. Transition metal complexes with η^3-diphosphaallyl were first prepared by reactions of the chlorophosphino-substituted methylenephosphine with sodium tetracarbonylcobaltrate [18]. These η^3-complexes can also be obtained with nickel and iron anionic complexes K[CpNi(CO)] and $Na_2[Fe(CO)_4]$ and they exist as a syn/anti isomer mixture for Ni [19].

3.1. *Structure of the η^1- and η^3-diphosphaallyl complexes*

The structure of the η^1- or η^3-complexes is unambiguously established by the ^{31}P NMR spectroscopic data. At 30°C, the ^{31}P resonance for the signals of the η^1-complexes are a low-field-shifted AB system ($274 < \delta < 350$) whereas the η^3-complex resonance is shifted to much higher fields ($5 < \delta < 65$) and the singlet signal, observed at room temperature, is the consequence of the equivalence of both phosphorus atoms (Table 1). As expected, for **3aB** further proof for the formation of a phosphorus–tungsten double bond is provided by the very large $^1J(PW)$ coupling constant of 700 Hz suggesting sp^2 hybridization of the phosphorus atom [20]. In contrast, tungsten complex **4bB** with full electron delocalization has a low $J(PW)$ coupling constant of 137 Hz. Also, the $\delta\ ^{13}C$ resonance of C_9 is a triplet, characteristic of a carbon atom coupled to two equivalent phosphorus atoms (**4bA**: 108.0, $^1J(CP) = 77$ Hz; **4bB**: 94.6, $^1J(CP) = 117$ Hz). The infrared spectra show two $\nu(CO)$ bands for molybdenum and tungsten com-



Scheme 4. Variable temperature ^{31}P NMR spectra of **3aA** in C_7D_8 at 32.44 MHz: (A) at −100°C; (B) at 30°C; (C) at 100°C.

plexes and a broad band for cobalt complexes.

3.2. Thermal lability of the diphosphaallyl complexes

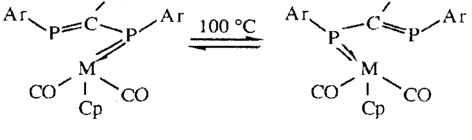
3.2.1. η^1-Diphosphaallyl complexes

The X-ray structure determination of Karsch [17] of the η^1-diphosphaallyl molybdenum complex described as a metalladiphosphabutadiene, indicates sp^2 hybridization of the two phosphorus atoms, and an (*s-trans*)-heterobutadiene framework. The two aryl substituents are nearly orthogonal to the PCP plane and are in exo–endo positions with respect to the PCP dihedral angle. In particular, the aryl group, bound to the phosphido-moiety is endo position and is parallel to P=C double bond. Furthermore, the ^2J(PP) coupling constant is 55 Hz. In our case, the η^1-diphosphaallyl complexes **3** are prepared either from diphosphiranes or from their photochemical isomers, the substituted 1,3-diphosphapropenes which have a *trans* configuration and a *gauche* conformation [10]. The complexation requires prolonged heating in toluene ($\geqslant 4$ h) in the presence of a large excess of anionic complex, whereas the Karsch allyl complexes were obtained easily in THF at room temperature. Moreover, the ^2J(PP) value is in the range of 110 Hz in complexes **3**, higher than in other phosphido-complexes [17]. They are also not stable and slowly decompose in solution during one week.

These differences of behaviour between our complexes **3** and those described in the literature can be explained by a different conformation of aryl substituents with respect to the PCP dihedral angle. The aryl groups must be exo–exo in complexes **3**. The ^{31}P NMR data of complexes **3** are temperature dependent (Scheme 4). Upon heating **3** in toluene, all the AB spectra coalesce and give a singlet. This is the consequence of fast exchange between the metal (in the endo position) and the two phosphorus atoms (Scheme 5). We also observed an analogous simplification of spectra of **3** at low temperature (-100°C). Presently, we have no good explanation for this surprising phenomenon.

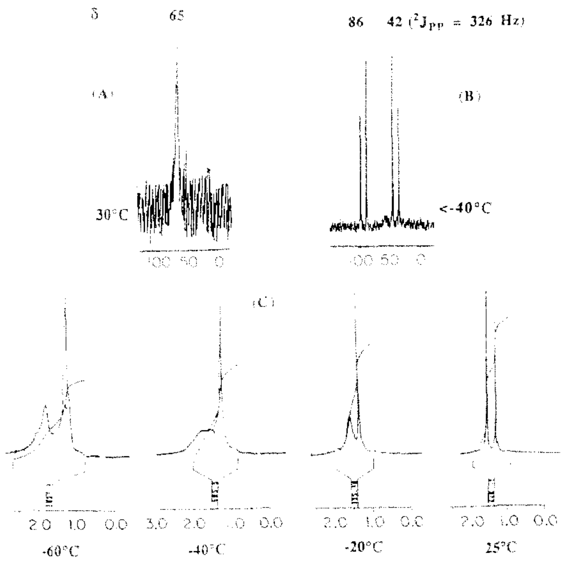
3.2.2. η^3-Diphosphaallyl complexes

The ^{31}P singlet signal of the η^3-complexes **4** in the temperature ranging from room temperature to +80°C, splits to an AB system at -40°C (Scheme 6, Table 2). Furthermore, the temperature-dependent ^{1}H-NMR spectra indicate the non-equivalence of the *ortho-tert*-butyl groups at low temperature (Scheme 6). They interchange has a $\Delta G^{\ddagger}$ of 15 kcal mol^{-1}. The anisotropy of the two phosphorus atoms can be explained by several hypotheses: (i) a *syn–anti* equilibrium of the η^3-allyl complexes with the aryl groups endo–exo and exo–exo with respect to the PCP dihedral angle, as described by Appel [19]; (ii) a hindrance to rotation about the metal–diphosphaallyl bond; and (iii) the distortion of the P–C$_{ipso}$ bond of aryl groups, out the PCP plane (Scheme 7). The first hypothesis, observed for η^3-diphosphaallyl nickel complexes, can be excluded because of the large ^2J(PP) values of **4** ($\cong 350$ Hz) compared to 8 and 34 Hz observed by Appel [19]. This ^2J(PP) exaltation is probably the consequence of the syn-position of the two phosphorus lone pairs [21]. For the second hypothesis, there are data to show conformational equilibrium for the η^3-allyl molybdenum complex due to the rotation about metal-ligand [22]. The recent X-ray structure of lithium diphosphaallyl is consistent with the last hypothesis because



3 **3**

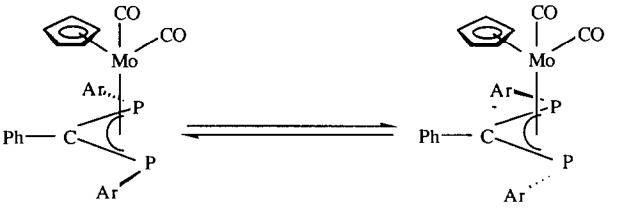
Scheme 5. Fast exchange between the metal and the two phosphorus atoms in the η^1-complexes **3** at 100°C.



Scheme 6. Variable temperature NMR spectra of **4bA** in C_7D_8: ^{31}P NMR at 32.44 MHz: (A) at 30°C; (B) at -40°C; (C) ^{1}H NMR at 200.13 MHz in the range of -60°C–25°C

TABLE 2. Variable temperature–^{31}P NMR parameters of the π-diphosphaallyl molybdenum and tungsten complexes **4b**

Complex	-40°C			30°C
	δ_A	δ_B	^2J(PP) (Hz)	δ
4bA	86	42	326	65
4bB	7	2	354	5



4bA **4bA**

Scheme 7. Anisotropy of the two phosphorus atoms in the η^3-complexes **4** at −40°C due to the presence of the two aryl substituents on either side of the PCP plane.

there are two aryl substituents on either side of the PCP plane [23]. The phenyl substituent on the carbon atom must induce a steric hindrance to the aryl groups and promote this geometry. At the moment, it is difficult to decide between these hypotheses.

The isomerization of the η^1-cobalt complex to the corresponding η^3-complex upon heating constitutes the first example of such an interconversion in the diphosphaallyl systems. No reversible reaction was observed although such an equilibrium (η^1-phosphaallyl) $\rightleftharpoons$ (η^3-phosphaallyl) has already been described for other systems by Mathey *et al.* [24].

The thermal lability of these complexes, **3** and **4**, is probably one reason for their instability and for the difficulties in obtaining single crystals.

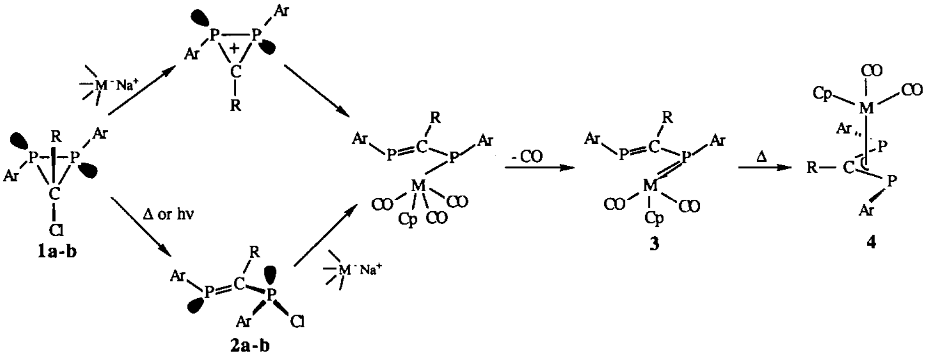
3.3. *Influence of the carbon atom substituents on the nature of the allylic complexes*

The formation of diphosphaallyl ligands is directly related to the nature of the carbon atom substituents. With R = Ph, we obtain only the η^3-complexes, whatever the nature of transition metal (M = Mo, W, or Co). The η^3-complexes are more stable than the η^1 (R = Me). This particular stabilization of allylic cation has already been suggested by Wiberg on the basis of *ab initio* calculations: π-electron delocalization is responsible for this stabilizing effect [25]. For a phenyl substituent (π-donor group), the formation of the more stable η^3-complexes is promoted, whereas a methyl substituent (σ-donor group) affords the η^1-complexes. The steric bulk of phenyl compared to methyl is presumably responsible for the thermal lability of these η^3-complexes, **4**.

3.4. *Mechanism*

The formation of the same diphosphaallyl complexes, **3** and **4**, from diphosphiranes **1** and from their photochemical isomers **2** raises the problem of mechanism. The reaction may occur either by initial attack of the anionic complex on diphosphirane *via* an unstable diphosphiranium cation followed by cationic ring-opening, or by prior thermal ring-opening of diphosphirane followed by coordination. Since the metallation reactions occur after prolonged heating, the latter mechanism is more likely. Moreover, the formation of the same complexes from *trans*-1,3-diphosphapropenes is also consistent with the latter mechanism.

Only the *trans*-isomers undergo metallation and the *cis*-isomers remain unchanged (by-products). Nevertheless, recent calculations [16,26] and experimental results [13,15,16] indicate that the thermal and cationic ring-opening of diphosphiranes (resulting from a homolytic or heterolytic rupture of the C–X bond followed by rupture of the P–P bond) leads to a mixture of cis and trans isomers by a disrotatory process. The complexation reactions undoubtedly result in initial formation of η^1-complexes (1-electron donor), which, in contrast to **3**, are not detectable. Instead, they undergo spontaneous loss of a carbonyl to give η^1-complexes **3** (3-electron donor). The σ-form is the first step of complexation. The transition from σ- to π-complexes is accompanied by a marked highfield shift of the ^{31}P NMR signal (Table 1), and the π-complexes constitute the last step of the reaction (Scheme 8). The formation of the η^1- or η^3-complexes is controlled by



Scheme 8. Mechanism of formation of the η^1- and η^3-complexes **3** and **4**.

the nature of the carbon substituents and the transition metal complexes.

4. Conclusion

The reaction of anionic transition metal complexes with functionalized diphosphiranes are, in comparison to those of 1,3-diphosphapropenes, relatively sluggish and require thermal activation. The reaction of monohalogenated diphosphiranes with anionic transition metal complexes occurs upon heating and leads to the σ- or π-diphosphaallyl complexes as a result of preferential P–P bond rupture, depending on the reaction conditions, the nature of the carbon substituents, and the transition metal complexes. π-donor substituents (R = Ph) promote the η^3-form, whereas σ-donor (R = Me) afford the η^1-complex. This new synthetic pathway leads for the first time to π-molybdenum and tungsten complexes. Furthermore, the σ-complexes have a conformation different from those already described. They are unstable upon standing, and an η^1- to η^3-thermal isomerization is shown by the cobalt complexes. The thermal lability of these diphosphaallyl complexes explains their instability. The monohalogenated 1,3-diphosphapropenes obtained by photochemical ring-opening of diphosphiranes lead to the same complexes. In contrast, the dihalogenated diphosphapropenes afford quantitatively the 1,3-diphosphaallene under the same conditions. These complexation reactions allow us to stabilize the 1,3-diphosphaallyl cations, which transform to a cyclic phosphonium phosphaalkene species in the absence of anionic complexes [13].

5. Experimental section

All reactions were performed under argon using Schlenk tube techniques. All solvents were reagent grade and were purified, dried and degassed by standard techniques. All commercially available reactants were used as received. The diphosphiranes **1a–d** and their photochemical isomers, the 1,3-diphosphapropenes **2a–d** were prepared according to the procedures already described [9,10]. NMR spectra were recorded on multinuclear AC 80, AC 200 and 250 WM Bruker spectrometers operating at 80.13, 200.13 and 250.13 (^{1}H), 20.15 (^{13}C) and 32.44 (^{31}P) MHz. Chemical shifts are downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are given in Hertz. Mass spectra were obtained either on Ribermag R1010 (DCI/NH_3) or Varian Mat 311A (FD) spectrometers. Infrared spectra were recorded on Beckman IR10 and Perkin-Elmer 225 spectrometers. Photochemical reactions were performed in a Rayonet photochemical reactor.

5.1. Preparation of the anionic transition metal complexes

The monomeric anionic complexes were obtained by reduction of the dimers with sodium amalgam. To the amalgam obtained at room temperature from sodium (0.054 g) and mercury (1 ml), were added freshly distilled THF (20 ml) then the dimer (0.8 mmol). The mixture changed from red to yellow. After decantation, the formation of the anionic complexes was checked by infrared spectroscopy. IR (THF):

A: $Na[CpMo(CO)_3]$ ν(CO) 1896, 1792 and 1743 cm^{-1};
B: $Na[CpW(CO)_3]$ ν(CO) 1892, 1788 and 1738 cm^{-1};
C: $Na[Co(CO)_4]$ ν(CO) 1883 and 1851 cm^{-1};
D: $Na[CpFe(CO)_2]$ ν(CO) 1900, 1800 and 1745 cm^{-1}.

5.2. General method for the synthesis of the 1,3-diphosphaallyl complexes

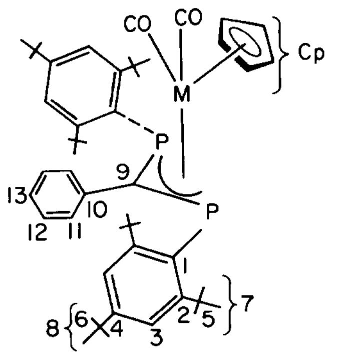
*5.2.1. From the diphosphiranes **1a,b***

To a stirred solution of diphosphiranes **1** (0.08 mmol) in THF (5 ml) was added *via* a syringe 10 molar eq. of complex **A** or **B** (M = Mo, or W). The mixture was stirred at room temperature for 10 min. The solvent was then evaporated to dryness and the residue taken up in toluene (20 ml). The solution was heated under reflux for 18 h. The progress of the reaction was followed by ^{31}P NMR spectroscopy. The mixture was allowed to cool to room temperature then filtered through Celite under argon. The diphosphaallyl complex was purified by successive recrystallization from pentane. The σ-allyl complexes **3** obtained as yellow oils, were unstable and decomposed in solution. The π-allyl complexes **4** were obtained by recrystallization from pentane at low temperature as red powders. The yields were 30–40%.

*5.2.2. From the 1,3-diphosphapropenes **2a,b***

To a stirred solution of **2** (0.16 mmol) in THF (5 ml) was added *via* a syringe 4 molar eq. of monomer complex **A** or **B** (M = Mo, or W). The mixture was stirred at room temperature for 10 min. The solvent was then evaporated to dryness and the residue taken up in toluene (20 ml). The solution was heated under reflux for 4 h. The progress of the reaction was followed by ^{31}P NMR spectroscopy. The mixture was allowed to cool to room temperature then filtered through Celite under argon. The diphosphaallyl complexes were purified according to the procedure described above. The yields were 70–80%.

3aA: ^{31}P NMR (C_7D_8) δ 331 (P_A), 327 (P_B), ^2J(PP) = 110 Hz. ^{1}H NMR (C_7D_8) δ 1.33 (s, 18H, *p*-^{t}Bu), 1.38 (s, 18H, *o*-^{t}Bu), 1.59 (s, 18H, *o*-^{t}Bu), 1.80 (m, 3H,



Me), 5.20 (s, 5H, Cp), 7.20 (m, 4H, Ar). IR (CH_2Cl_2) ν(CO) 1925 and 1852 cm^{-1} (broad). MS (FD) $C_{45}H_{66}O_2P_2Mo$, m/z 798 (M^+, ^{98}Mo). UV (toluene) λ 432 nm.

3aB: ^{31}P NMR (C_7D_8) δ 328(P_A), 274 (P_B), $^2J(PP) = 112$ Hz, $^1J(PW) = 700$ Hz. ^1H NMR (C_7D_8) δ 1.30 (s, 18H, p-^tBu), 1.50 (broad s, 36H, o-^tBu), 1.78 (broad m, 3H, Me), 5.25 (s, 5H, Cp), 7.30 (m, 4H, Ar). IR (CH_2Cl_2) ν(CO) 1916 and 1835 cm^{-1} (broad). MS (DCI/NH_3)$C_{45}H_{66}O_2P_2W$, m/z 885 ($M^+ + 1$, ^{184}W).

4bA: ^{31}P NMR ($CDCl_3$) δ 65 (broad). ^1H NMR ($CDCl_3$) δ 1.23 (s, 18H, p-^tBu), 1.36 (s, 36H, o-^tBu), 5.4 (s, 5H, Cp), 6.4 (m, 5H, Ph), 7.2 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ 201.0 (m, CO), 157.2 (s, C_2), 150.2 (s, C_4), 141.0 (broad s, C_{10}), 132.7 (d, $^1J(CP) = 57$ Hz, C_1), 127.0 (s, C_{13}), 126.6 (s, C_{12}), 124.8 (s, C_{11}), 123.4 (m, C_3), 108.0 (t, $J(CP) = 77$Hz, C_9), 93.3 (s, Cp), 39.5 (s, C_5), 34.7 (s, C_6), 33.6 (s, C_7), 31.2 (s, C_8). IR (CH_2Cl_2) ν(CO) 1944 and 1871 cm^{-1}. MS (DCI/NH_3) $C_{50}H_{68}O_2P_2Mo$, m/z 861 ($M^+ + 1$, ^{98}Mo).

4bB: ^{31}P NMR ($CDCl_3$) δ 5.1 (sharp), $J(P\text{-}W) = 137$ Hz. ^1H NMR (C_7D_8) δ 1.35 (s, 9H, p-^tBu), 1.39 (s, 9H, p-^tBu), 1.59 (s, 36H, o-^tBu), 5.30 (s, 5H, Cp), 6.60 (m, 5H, Ph), 7.20 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ 213.9 (s, CO), 204.0 (s, CO), 157.7 (s, C_2), 157.1 (s, C_2), 150.3 (s, C_4), 144.1 (broad s, C_{10}), 132.8 (d, $J = 68.6$ Hz, C_1), 128.7 (m, C_1), 126.7 (s, C_{13}), 126.5 (s, C_{12}), 124.6 (s, C_{11}), 123.0 (s, C_3), 120.9 (s, C_3), 119.5 (s, C_3), 94.6 (t, $J(CP) = 117$ Hz, C_9), 92.0 (s, Cp), 39.3 (s, C_5), 34.7 (s, C_6), 34.2 (s, C_6), 33.9 (s, C_7), 33.5 (s, C_7), 31.3 (s, C_8). IR (CH_2Cl_2) ν(CO) 1951 and 1900 cm^{-1}. MS (DCI/NH_3) $C_{50}H_{68}O_2P_2W$, m/z 947 ($M^+ + 1$, ^{184}W). UV (CH_2Cl_2) λ 508 nm.

5.3. *Synthesis of the 1,3-diphosphaallyl cobalt complexes*

To a stirred solution of **2a** (0.1 mmol) in THF (5 ml) was added an excess of Na[Co(CO)$_4$], **C** (4 molar eq). The mixture was heated at 45°C for 3 h and then the solution was evaporated to dryness. The residue was taken up in pentane and filtered through Celite under argon. The filtrate was concentrated and **3aC** was obtained as a yellow oil in 30% yield. **3aC** was also obtained after stirring the THF solution at room temperature for 10 min. Then the solution was evaporated to dryness and the residue taken up in toluene (20 ml). Heating of the toluene solution at 50°C for 1 h afforded the (η^1-diphosphaallyl) cobalt complex **3aC** in 35% yield. However, upon heating in refluxing toluene for 3 h, the phosphido-cobalt complex **3aC** is irreversibly transformed into the π-allylic complex **4aC**. This thermal lability was observed solely for the cobalt complexes, and could explain our difficulties concerning their purification and their stability.

3aC: ^{31}P NMR (C_6D_6) δ 350 (broad s). IR (CH_2Cl_2) ν(CO) 2015 cm^{-1} (broad).

4aC: ^{31}P NMR ($CDCl_3$) δ 61. IR (CH_2Cl_2) ν(CO) 1970, 1994, and 2007 cm^{-1}

4bC: ^{31}P NMR ($CDCl_3$) δ 64. IR (CH_2Cl_2) ν(CO) 1990 cm^{-1} (broad). MS (DCI/NH_3) $C_{46}H_{63}O_3P_2Co$, m/z 729 ([$M^+ + 1$]-2 CO).

5.4. *Synthesis of the reduced 1,3-diphosphapropenes 5*

5.4.1. *From the diphosphiranes 1a,b*

To a solution of the diphosphiranes **1** (0.1 mmol) in THF (10 ml) was added 8 molar eq. of anionic iron complex in THF. The mixture was stirred at room temperature for 15 min, then the solution was evaporated to dryness. The residue was taken up in toluene (20 ml) and heated at reflux for 2 h. The mixture was filtered through Celite and purified by recrystallization from hexane at low temperature leading to **5a,b** in 80% yield.

5.4.2. *From the 1,3-diphosphapropenes 2a,b*

To a solution of the 1,3-diphosphapropenes **2** (0.1 mmol) in THF (20 ml) was added 2 molar eq. of iron anionic complex monomer in THF. The mixture was stirred at room temperature for 1 h, then it was filtered through Celite. **5a,b** was obtained after purification in 80–90% yield.

5a: ^{31}P NMR (C_7D_8) δ 259 (P_A); -45 (P_X); $^2J(PP) = 192$ Hz; $^1J(PH) = 230$ Hz. MS (DCI/NH_3) $C_{38}H_{62}P_2$ m/z 581 ($M^+ + 1$).

5b: ^{31}P NMR (C_7D_8) δ 260 (P_A); -33 (P_X); $^2J(PP) = 128$ Hz; $^1J(PH) = 233$ Hz. MS (DCI/NH_3) $C_{43}H_{64}P_2$ m/z 643 ($M^+ + 1$).

5.5. *Synthesis of the 1,3-diphosphaallene 6*

5.5.1. *From the gem-dihalogenodiphosphiranes 1c,d*

To a stirred solution of **1** (0.15 mmol) in THF (5 ml), was added 10 molar eq. of monomer complexes **A**, **B**, **C**, or **D** (M = Mo, W, Co, or Fe). After stirring at room temperature for 10 min, the solution was evaporated to dryness. Toluene (20 ml) was added and the solution was heated at reflux for 8 h. After filtration through Celite, the filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography on silica (eluent: hexane). Light yellow crystals of **6** were obtained in 70% yield. The spectroscopic data were in good agreement with the literature data [11,27].

5.5.2. From the 1,3-diphosphapropenes ***2c,d***

To a stirred solution of **2** (0.14 mmol) in THF (5 ml), was added 4 molar eq. of monomers (M = Mo, W, Co, or Fe). After stirring at room temperature for 2 h, the solution was evaporated to dryness. The residue was taken up in hexane then filtered through Celite. The filtrate was concentrated *in vacuo* and the crude product was purified according to the previously described procedure. **6** was obtained in 90% yield.

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